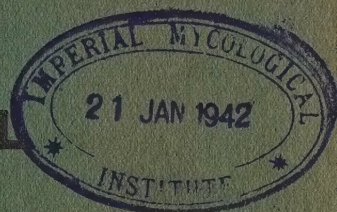


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THE ABSORPTION OF WATER BY RUBBER

PART I

METHODS OF EVALUATION

BY

V. H. WENTWORTH

Summary

A description is given of the methods in use at the Rubber Research Institute of Malaya for determining the water-absorption capacity of crude and vulcanised rubber either by suspension in water-vapour or by immersion in water.

Amplification of published methods of testing by immersion was found to be desirable and procedures applicable to crude rubber in any form are described.

An examination has been made of the influence on the results of the individual operations involved and the conditions under which the tests are carried out.

Numerous procedures have been suggested for estimating the water-absorption capacity of crude rubber. These are based mainly upon the determination of the increase in weight of samples either after suspension in air of known humidity or after immersion in water at standard temperatures for fixed periods of time. The tendency has been for workers in Europe to adopt the former method whereas the latter method is favoured in America.

In general, simplicity of technique is the attribute of water-vapour tests although it is probable that absorption of water solely in the form of vapour does not present a serious technical problem. Testing by both methods requires more elaborate apparatus for the preparation of test-pieces than is likely to be freely available in rubber-producing countries, although a smooth roll creping machine, if in good condition, might be used without a water spray to prepare a thin sheet for testing in water vapour. It is believed that a sufficiently good correlation exists between tests upon the crude and manufactured product to enable a safe standard to be set for the crude material but as in all such problems, service trials are the true criteria.

It is not the purpose of this paper to attempt to select one method of testing to the exclusion of another but rather to set out practical details for carrying out the tests and to specify the methods used in the Rubber Research Institute.

SUSPENSION-IN-VAPOUR METHODS

Cooper and Daynes (1936) examined two methods previously used by Lowry and Kohman involving the suspension of the sample in water vapour and concluded that the direct measurement of the increase in weight of a rubber sample suspended in vapour was the most convenient method for repetition work, although they considered that a method in which unabsorbed water vapour was estimated by vapour pressure measurements was more accurate. Testing in vapour was also described by Skinner and Drakeley (1932) and theoretical aspects were discussed by Daynes (1937); Tadao Okita (1937) preferred to test in vapour rather than liquid because he considered the method was both more convenient and less liable to errors from oxidation.

The amount of water vapour absorbed within a given time is dependent upon the surface exposed and Skinner and Drakeley (1932) concluded that " . . . comparable results are only obtained in a reasonable time by using shredded samples of rubber." Using the method of shredding described by these authors (which is to pass the sample of rubber through a tightly closed mill with one roll stationary) the writer was unable to confirm their conclusion and found that, with the equipment at his disposal, a thin sheet was preferable to shreds. Further, it is more difficult to ensure the same degree of subdivision between shredded samples, whereas a sheet can be prepared within specified limits of thickness or weight per unit area.

Table I gives the absorption results obtained from six test-pieces prepared either in sheet or shredded form from the same rubber sample after remaining in the same atmosphere of 84 per cent humidity at 90°F. for eight days. The shredding was carried out on a 12-inch mill of roll diameter six inches, using a tightly closed nip. The front roll was not driven and the back roll revolved at 18½ r.p.m.

TABLE I

Absorption of Water-vapour by Sheeted and Shredded Rubber

Form of rubber	Absorption (per cent)						Mean
Sheeted ...	.495	.486	.477	.472	.467	.463	.477
Shredded ...	.477	.446	.442	.432	.429	.418	.441

The results in Table I show that shredding as described gives less absorption than sheeting after eight days exposure although attempts were made to obtain the maximum surface by shredding as finely as possible.

A method of testing in water-vapour has been used by the London Advisory Committee for Rubber Research (L.A.C.) for a considerable time but only brief details have been published (Martin, Davey, Baker and Rhodes 1934). The Rubber Research Institute of Malaya (R.R.I.M.) has adopted the method, with slight modifications. In dealing with crude rubber the method seems as satisfactory as any of the published methods and the details of the test, as used in the R.R.I.M., are as follows.

The L.A.C.-R.R.I.M. vapour test for water absorption

1. Pass the sample of crude rubber twice through a cold mill having tightly closed rolls, to produce a uniform thin sheet.
2. Using a Schopper circular knife (diam. 4.46 cm.), cut from the sheet the desired number of test-pieces. Four test-pieces per sample are usually taken.
3. Place in a closed container over a saturated solution of potassium chloride in a constant temperature room at 90°F. for eight days. The relative humidity is approximately 84 per cent. (Spencer 1926; Leopold and Johnstone 1927).
(The containers in use are specimen jars ten inches high and seven inches in diameter, in which three wooden uprights hold eight sliding frames with threads stretched across, each frame carrying four discs of rubber.)
4. After eight days, remove the discs individually and weigh immediately.
5. Place in an oven maintained at about 90°C. and dry to minimum weight (about four hours).
6. Calculate the result as follows

$$\text{Absorption} = \frac{\text{Wt. of wet disc} - \text{Wt. of dry disc}}{\text{Wt. of dry disc}} \times 100\%$$

The British Standards Institution has now published its "Methods of Testing Latex, Raw Rubber and Unvulcanised Compounded Rubber" (No. 902—1940) and the method of evaluating the "equilibrium water absorption" is very similar to the method described above. The differences are the use of one test-piece of

TABLE II

The influence of thickness upon the absorption of water-vapour by sheeted rubber

No.	Weight per 16 sq. cm. gm.	Water-absorption from Vapour (per cent)	
		Dried 4 hours @ 70°C.	Dried further 4 hrs. @ 90°C.
1	0.45	0.45	0.54
2	0.55	0.54	0.65
3	0.57	0.51	0.69
4	0.68	0.54	0.70
5	0.72	0.53	0.81*
6	0.72	0.50	0.58
7	0.95	0.59	0.63
8	1.13	0.53	0.60
9	1.21	0.58	0.61
10	1.21	0.58	0.63
11	1.23	0.56	0.64
12	1.25	0.54	0.59
Average		0.54	0.62
13	1.52	0.61	0.74
14	1.56	0.65	0.66
15	1.67	0.64	0.70
16	1.79	0.62	0.77
17	1.83	0.62	0.75
18	1.84	0.59	0.71
19	2.54	0.64	0.68
20	2.54	0.63	0.68
21	2.58	0.63	0.65
22	2.58	0.63	0.68
23	2.84	0.62	0.65
24	2.87	0.63	0.67
Average		0.63	0.69

* not included in average

about four times the area instead of four separate test-pieces, the specification of a test-piece thickness of one gram per 16 sq. cm. and the expression of the result as a percentage by volume instead of by weight (the above calculation can be corrected by multiplying by the density of the rubber).

The British Standards Institution method specifies that the test-sheet shall weigh approximately one gram per 16 sq. cm. and experiments were made to examine the effect of varying the thickness, since the mill at our disposal will not produce a sheet meeting this requirement except by inserting small pieces of rubber from which only one disc can be cut. Twenty-four discs were prepared from the same sample of rubber, increasing thicknesses being obtained by opening the "nip" of the mill. The discs were kept under the specified conditions for eight days and were then weighed. As a matter of interest drying was carried out in two stages—for four hours at 70°C., followed by a further four hours at 90°C.—and the discs were re-weighed after each period with the results given in Table II.

From these results it is seen that the thicker discs give higher absorption results than the thinner ones and there is therefore no fear of under-estimation when using apparatus which will not produce a sheet of the requisite thinness. It is possible that the reason for this is to be found in the greater masticating effect which occurs when preparing the thinner sheet and which is examined later in this paper.

Drying should be at 90°C. and not 70°C. despite the fact that ovens maintained at the latter temperature are more common in rubber testing laboratories.

WATER-IMMERSION METHODS

Messenger and Scott (1936) tested sole crepe by immersion in water but the laminated nature of the material led to results not entirely due to the characteristics of the rubber. Daynes (1937) rejected the liquid-immersion test because it required too long to reach a stage approaching saturation but judging by its wide use it is evident that the test is considered suitable for comparative purposes.

Boggs and Blake (1926; 1936) proposed a method of testing which has received fairly wide adoption in its general form although the details have been amplified and slightly modified by Noble (1936; 1938) and others (B.P. 484,659). In broad outline, the "Boggs and Blake" test consists of moulding the rubber sample by heat and pressure to uniform dimensions, weighing the specimen, immersing in water at 70°C. for 20 hours, drying the surface and

re-weighing. The increase in weight is expressed as milligrams of water absorbed per square inch of surface, a method of expression which is to be preferred to that of percentage absorption by weight for specimens of appreciable thickness because, as was demonstrated by Rowell (1938) using Tufnol sheets, misleading conclusions can be drawn by reporting the results in this manner.

Van Dalfsen (1939) has suggested the use of an immersion test differing widely from the earlier methods but it is considered that there is no reason to justify a wide deviation from the outline of the "Boggs and Blake" procedure for the general classification of crude rubber, even though the facilities available may make it necessary to modify details. It is probable however that consumers, in particular, will use additional tests more closely resembling the service conditions their products have to meet. With this in mind, tests are also made at the R.R.I.M. by immersing for 14 days at 90°F.—a tropical atmospheric temperature—in addition to 20 hours at 70°C.

The influence of different factors on the resistance of crude rubber to the absorption of water has been discussed by several authors. Evidence that oxidation increases the water-absorption capacity of rubber was put forward by Tadao Okita (1937) Blake and Morss (1938) and Robertson (1938). Boggs and Blake (1936) considered that deproteinised rubber resisted oxidation as satisfactorily as normal rubber but they observed considerable degradation of the rubber when the period of immersion was increased. Contradictory evidence has been reported by Soule (1931) who exposed ribbed smoked sheet to extremely drastic conditions without deterioration. He suggested that the preliminary heating of the rubber involved in the Boggs and Blake method of preparing the samples for testing might have reduced its resistance. The work of Kemp (1937), however, did not support this view; referring to plantation smoked sheet he stated that "if the sheets are heated in the press at 142°C. for 1.5 hours, the rubber absorbs less water and becomes electrically more stable." This he attributed to heat hardening of the proteins; he also found that mastication was beneficial in improving the resistance to water absorption. It was evident therefore that the preliminary treatment necessary for the preparation of the sample should be carefully controlled if its subsequent behaviour on immersion in water is affected.

In order to apply the Boggs and Blake method of testing to rubber in any form, whilst utilising available apparatus, a technique has been developed which is described in this paper together with an account of the effects of the various factors in the procedure upon the results obtained.

THE PREPARATION OF TEST-PIECES

In general, raw rubber to be tested for water absorption is in the form of thin crepe which can be plied up to any desired thickness without a preliminary treatment, but if smoked sheet or sole crepe has to be tested the preparation of test-pieces of a standard thickness usually involves mastication of the rubber, which is undesirable. To avoid this difficulty a method of testing applicable to raw rubber in any form was devised, with as little variation as possible from the method of Boggs and Blake.

In the Boggs and Blake procedure as described in B.P. 484,659 (U.S.P. 2,123,862) and by Noble (1936) the requisite number of crepe layers are placed between aluminium sheets in a frame 0.08 inch thick and are held in a platten press at 215°F. for 30 minutes. The rubber is allowed to cool in the mould and after removal the sheet assumes a thickness of about 2.25 mm. (0.089 inch) from which test-pieces of size 4×1 inches are cut. Preliminary trials were carried out on the basis of these instructions and steel moulds, without spew-ways, having an inserted aluminium base plate and an aluminium top plate were obtained, the size of the moulds being intended to produce three test-pieces.

The press available for this work was a 12×16 inches steam-heated platten press, operated by hand screw. For practical reasons it was found convenient to use it at 259°F. (20 lb./sq. in. steam) instead of 215°F. (1 lb./sq. in. steam) but the influence of temperature was one of the factors investigated before adopting the higher temperature.

Various types of rubber were pressed but the mouldings were disappointing. The best results were obtained from blanks which almost filled the cavity and flowed very little. When pressing smoked sheet and sole crepe the thickness could not be adjusted and it was often necessary for a weighed blank to flow considerably, as a result of which moulding proved to be unsatisfactory. Spew-holes of various sizes were cut in the moulds and these effected some improvement but when a satisfactory moulding was apparently obtained, pronounced shrinkage occurred along the flow lines some time after the removal of the sample from the mould. Twenty-four hours later only one test-piece of correct size could be cut from a moulding intended for three. A temporary improvement resulted from keeping the rubber in the mould for 24 hours, although it only postponed the distortion, which occurred after the test-piece had been cut to the correct size and immersed in water.

A reduction of plasticity and "nerve" by mastication was another expedient which assisted moulding but the effect was

only temporary and the sheet subsequently developed a very uneven surface and was distorted. The use of any form of mould lubricant was considered to be undesirable.

It was found that much better test-pieces could be obtained by pressing the rubber between aluminium plates, without the restriction of a mould, and this proved to be the best method for rubber in any form but the thicknesses of the resultant sheets varied. Allowances had to be made for these variations in the calculation of results. Although this method of pressing is well suited to a screw-type press distance pieces may be required when using a press having a continuous hydraulic pressure.

The sheet was required to be of sufficient size for the cutting of six test-pieces each measuring 4×1 inches. Having adopted the above method of pressing, twenty-four aluminium plates size $11 \times 9\frac{1}{2} \times 0.125$ inches were obtained to allow for the preparation of one dozen sheets per day. Smoked sheet, sole crepe, and thin pale crepe were cut to a size of $10 \times 4\frac{1}{2}$ inches, plied up when necessary, and placed between pairs of plates together with an embossed aluminium identification tag. Each sample was pressed separately for 30 minutes at 259°F. and the press was re-tightened after 15 minutes. On removal from the press, the aluminium sheets were not separated but were cooled under the tap and placed under light pressure overnight in a small screw press of the office type. Test-pieces were then conveniently prepared from the smooth pressed sheets by placing them on parchment paper and cutting to a size of 4×1 inches on a photographic trimming board.

FACTORS INVOLVED IN TESTING BY THE IMMERSION METHOD

(a) *The effect of the temperature of pressing on water absorption*

In published descriptions of the immersion test a temperature of 215°F. (1 lb./sq. inch steam pressure) has been prescribed for the press but this was inconvenient with the apparatus at our disposal and it was desired to use a steam pressure of 20 lb. per sq. inch, if the results were not impaired. To examine the effect of press temperature, test-pieces were prepared by pressing at atmospheric temperature (85°F.), at 259°F. (20 lb. per sq. inch) and at 307°F. (60 lb. per sq. inch). Neither ribbed sheet nor crepe was suitable for this particular test, since cold pressing was not capable of producing a smooth sheet, and a special batch of rubber was prepared for the purpose. The coagulum was quite normal but during the machining the final marking rolls of the sheeting battery were not used. The smooth sheet, free from ribbing, was dried in a smoke-house,

Samples were tested by immersion in water at 70°C. for 20 hours and at 90°F. for 14 days, with the results given in Table III.

TABLE III

The effect of press temperature on water absorption

Temperature of pressing	Mean absorption (mg./sq. in)	
	20 hrs. at 70°C.	14 days at 90°F.
Approximately 85°F. (Atmospheric temperature) 	25.7	39.4
259°F. (20 lb./sq. in. steam) 	25.6	37.6
307°F. (60 lb./sq. in. steam) 	27.0	39.8

For practical purposes it appears that the results are not materially affected by the temperature of pressing used in the preparation of the test-pieces under either of the conditions of immersion; a temperature of 259°F. may be used instead of 215°F. without prejudice to the results.

(b) *The effect of mastication on water absorption*

As reported under "Preparation of test-pieces," mastication prior to moulding proved useful as an adjunct to moulding but the test-pieces were subject to delayed distortion. The treatment found to be suitable for general use with the minimum amount of working was to pass the rubber 30 times through a nip of 0.020 inch in a 12×6 inches mill having a differential of 1.4 and having the rolls at a temperature of 50°C. After pressing, the mould was cooled in water but was left unopened for 24 hours until just prior to cutting the test-pieces from the moulded sheet.

In Kemp's (1937) method of testing, mastication for ten minutes and pressing between cellophane sheets was prescribed but the author stated that mastication gave a beneficial effect. The data in Table IV verify this statement.

It was considered undesirable to submit samples to any treatment which reduces their water-absorption capacity and it is useful to provide a safety margin by ensuring that test figures represent maxima. In addition, mastication conditions are difficult to define and the necessary equipment is not usually available to rubber producers.

In examining the effect of mastication on water absorption, pressing between aluminium sheets was used without moulds and the first tests were carried out on air-dried sheet with a normal nitrogen content of 0.32 per cent.

Sufficient rubber to provide twenty-four test-pieces was divided into two parts. One part was masticated as previously described and the other did not receive any pre-treatment. After pressing at 259°F. twelve test-pieces were cut from both the milled and unmilled rubber and six tests of each rubber were made under two different conditions of immersion. The results are given in Table IV.

TABLE IV

The effect of mastication on water absorption

Conditions of immersion	Mean absorption (mg./sq. in.)	
	Un-masticated rubber	Masticated rubber
20 hrs. at 70°C. ...	24.3	16.1
14 days at 90°F.	30.3	17.0

The benefit of mastication is plainly evident, having reduced the water absorption by 36 and 44 per cent respectively in the short and long period tests. This benefit will accrue in the course of manufacture with the rubber and will serve as a margin of safety over test figures obtained on the crude rubber if mastication is avoided during testing.

In general, rubber to be tested for water absorption is in the form of crepe which has been subjected to a limited amount of mechanical working during manufacture. It was of interest therefore to examine the effect of mastication upon sole crepe and also upon a crepe of low nitrogen content. The latter rubber was prepared from latex which was treated with caustic soda, subsequently creamed, coagulated and the coagulum creped.

Table V gives the mean absorption from groups of three test-pieces.

Mastication of the sole crepe reduced the results by 13 and 19 per cent respectively in the short and long period tests. The effect on crepe of low nitrogen content was small.

TABLE V

The effect of mastication on the water absorption of crepe of medium and low nitrogen content

Conditions of immersion	Sole crepe (Nitrogen 0.26 per cent.)		Low-N crepe (Nitrogen 0.06 per cent.)	
	Mean absorption (mg./sq. in.)		Mean absorption (mg./sq. in.)	
	Un-masticated	Masticated	Un-masticated	Masticated
20 hours at 70°C.	16.2	14.1	5.9	5.4
14 days at 90°F.	28.1	22.7	8.8	8.6

THE IMMERSION OF TEST-PIECES

(a) *Method*

The following practical details have proved satisfactory. Each test-piece is immersed in distilled water in a $6 \times 1\frac{1}{2}$ inches test-tube covered by a watch glass and retained below the surface of the water by means of a sinker made by fusing a hook to the side of a glass rod. The test-piece is pierced by the hook near one end, causing the rubber to float vertically and completely immersed as shown in the figure. By this means, any tendency of the rubber to curl up on itself is eliminated. The tubes are conveniently contained in racks to hold six. By the use of individual containers labelling is facilitated and estimations of extracted material can be carried out by evaporation of the water.

Fig. 1



At the end of the test the samples are removed from the water one by one, wiped dry with a lintless cloth and weighed within two minutes. They are then left in an oven at 90°C. overnight and re-weighed when dry. By using this latter weight instead of the weight of the original test-piece, losses due to leaching out of water solubles are minimised and the moisture content of the sample prior to immersion is included.

(b) *The effect of the volume of water in which a test-piece is immersed*

If the surface of a rubber test-piece acts as a semi-permeable membrane and absorption is in part due to different osmotic conditions on either side of the membrane it is possible that variations might result from differences in the concentration of soluble material leached from the rubber into large or small volumes of water. It is known also that the absorption of water from a salt solution is less than that from distilled water [Boggs and Blake (1926); Messenger and Scott (1936)].

To examine the possible effects of different volumes of water a thin sheet of sole crepe was pressed and from it eighteen test-pieces were cut. Groups of three were tested in different volumes of water, each test-piece having a separate container. The results are given in Table VI.

TABLE VI

The effect of the volume of water on absorption

Volume of water in which each test-piece was immersed ml.	Immersed for 20 hours at 70°C.		Immersed for 14 days at 90°F.	
	Mean gauge of three test-pieces inch	Mean absorption (mg./sq. in.)	Mean gauge of three test-pieces inch	Mean absorption (mg./sq. in.)
120	.081	12.8	.077	18.1
250	.080	12.8	.079	18.5
500	.083	12.8	.075	18.3

The figures in Table VI indicate that the volume of water used in the test need not be closely specified. A convenient quantity is 120 ml., contained in a 6×1½ inches test tube.

(c) *The effect of the temperature of the water on absorption*

A thermostatically-controlled electrically-heated oven was used for this examination. Reliance was placed upon convection currents to circulate air within the oven and the temperature was

read on a mercury thermometer protruding through the top, the reading of which was set to $70^{\circ}\text{C.} \pm 1^{\circ}\text{C.}$

A rack of six tubes containing test-pieces was inserted in the oven from back to front. Each test-piece was cut from the same sheet of pressed crepe rubber. Twenty hours later the temperatures of the water in the tubes were recorded and were found to have a range of 12°C. from front to back. The water absorption of each test-piece was then determined and large differences were found. The results are shown in Table VII.

TABLE VII

The effect of water temperature on absorption

Mean gauge of test-piece (inch)	Temperature of water ($^{\circ}\text{C.}$)	Absorption after 20 hours (mg./sq. in.)
0.077	77	15.8
0.076	74	15.0
0.075	70	13.8
0.074	68	13.3
0.080	67	13.0
0.079	65	12.9

The results in Table VII show that the accurate control of the temperature of the water in which the samples are immersed is important; and an oven with positive circulation of air, in addition to a good thermostat, is necessary to ensure this. It is desirable to check the temperature of the water as well as that of the air in the oven. The temperature of the water should be 70°C. before the immersion of the test-pieces.

THE CALCULATION OF WATER ABSORPTION

In its simple form the calculation of the water absorption per unit area is derived from $\frac{\text{Weight of water absorbed}}{\text{Total area of test-piece}}$ but in practice this is modified to take into account the shrinkage of the test-piece. All test-pieces show some change of shape during immersion and as a general rule this takes the form of a shrinkage in length, with an increase in thickness except in cases in which the rubber is so prone to oxidation and softening that its own buoyancy

stretches it lengthwise when immersed vertically. By the methods of preparation recommended in this paper almost all test-pieces retain an approximately rectangular form, and it can be assumed as an approximation that the initial surface area of about nine square inches (which includes the area of the edges) is reduced during immersion to about eight square inches. The effective surface area is indefinite but for the purposes of calculation Noble (1936) assumes it to be eight square inches for test-pieces about 0.09 inch thick; that is, the loss in effective area due to shrinkage is taken to be approximately equal to the original area of the edges. Since it is probable that this procedure is widely used and because it is admitted that the whole test is one which cannot claim to have great accuracy or give absolute results, it is proposed to adopt eight square inches as the basic surface area for the purpose of calculation when testing crude rubber. Shrinkage is not a problem with vulcanised rubber and no such broad approximation is necessary.

Having regard to the approximation for shrinkage, small differences in thickness are unimportant but since the test-pieces prepared by the methods described may have thicknesses up to 0.25 inch in the case of thick sole crepe or other laminated crepe, a correction must be applied to cover such cases.

The method used is to adopt a thickness of 0.09 inch as a standard, apply a correction for any variation from this thickness and combine the gain or loss in edge area due to this adjustment with the basic area of eight square inches. Then, if "t" is the mean gauge of a test-piece, $10(t-0.09)$ is the excess edge area to be added to the basic area. If W is the weight of water absorbed in milligrams,

$$\begin{aligned}\text{Absorption} &= \frac{W}{8 + 10(t-0.09)} \\ &= \frac{W}{7.1 + 10t} \text{ mg./sq. in}\end{aligned}$$

THE RELIABILITY OF THE EDGE CORRECTION

It was desired to examine experimentally whether the suggested formula gave a reliable correction over a range of thicknesses and for this purpose, sheets of different thickness were prepared from one sample of rubber.

In order to ensure uniformity, masticated rubber of different thickness was used in preference to plied-up crepe. A sample of sole crepe was selected and masticated by passing thirty times through a mill as previously described, with the exception that

after twenty-eight passes the nip was re-set. The last two passes determined the thickness of the sheet and consequently of the test-piece after pressing. Three tests of each gauge were made under two conditions of immersion, with the results given in Table VIII.

TABLE VIII

The effect of thickness of test-piece on water absorption

20 hours at 70°C.		14 days at 90°F.	
Mean gauge of three test-pieces (inch)	Mean absorption of three test-pieces (mg./sq. in.)	Mean gauge of three test-pieces (inch)	Mean absorption of three test-pieces (mg./sq. in.)
.083	15.7	.080	25.3
.106	15.9	.108	25.4
.133	15.1	.142	25.8
.167	16.2	.159	26.0

The mastication of the rubber produced some distortion during immersion which is normally avoided by using un-masticated rubber but from these results it is considered that the suggested correction for gauge is adequate to permit of comparison between the results obtained with test-pieces of different thickness, having regard to the nature of the test.

Having examined the effects of individual factors in the procedure, the following is a summary of the practical details of the test.

THE R.R.I.M. MODIFICATION OF THE BOGGS AND BLAKE IMMERSION TEST

- (1) To prepare six test-pieces, cut the rubber sample in the shape of a rectangle of approximately $10 \times 4\frac{1}{2}$ inches. If thin crepe, ply-up sufficiently to produce a pressed sheet about 0.1 inch thick.
- (2) Place between aluminium sheets (size $11 \times 9\frac{1}{2}$ inches), together with an embossed aluminium identification tag.
- (3) Insert the "sandwich" in a screw-type platten press and hold at 259°C. (20 lb./sq. in. steam) for 30 minutes.
- (4) Remove and cool the aluminium sheets under a running tap without separating them from the rubber.

- (5) Place in an office-type hand press under light pressure for 24 hours.
- (6) Remove the rubber and place on parchment paper. Cut test-pieces to a size of 4×1 inches (trimming board or die).
- (7) Determine the mean gauge of each test-piece by taking about ten readings along the length of each.
- (8) Attach each test-piece to a glass sinker and immerse in distilled water previously brought to the testing temperature.
- (9) Keep in a thermostatically-controlled atmosphere for 20 hours at 70°C.; and/or for 14 days at 90°F.
- (10) Allow the tubes and contents to cool at atmospheric temperature for about half an hour, or cool in any convenient manner to avoid losses when weighing.
- (11) Remove each test-piece just prior to weighing; wipe dry with a lintless cloth and weigh within two minutes.
- (12) Place in an oven maintained at about 90°C. until dry and re-weigh.
- (12) Calculate the result from the formula:—

$$\left. \begin{array}{l} \text{Water absorption in} \\ \text{mg./sq. in. of surface} \end{array} \right\} = \frac{W}{7.1 + 10t}$$

where t is the mean gauge of test-piece in inches and W is the decrease of weight on drying in milligrams.

Testing by Immersion of Vulcanised Rubber

Since rubber in the unvulcanised state is rarely called upon to perform exacting functions, it is desirable that tests should also be made after vulcanisation. For this purpose the "Captax" mixing of the Crude Rubber Committee of the American Chemical Society (1939) was selected because it contains a high proportion of rubber and is also in common use for rubber testing. The formula is

Rubber	...	...	...	100.0
Mercaptobenzthiazole (Captax)	...	...	...	0.5
Stearic Acid	...	...	...	0.5
Zinc Oxide	...	...	...	6.0
Sulphur	...	...	...	3.5
				110.5

The curing temperature is 127°C. and a 60-minutes cure has been selected for comparative routine work in water-absorption testing.

Van Dalfsen (1939) did not recommend the use of this mix for water-absorption testing, despite his finding that out of four mixes which he examined " . . . only in the mixture accelerated by mercaptobenzothiazole did it (purified rubber) behave like normal rubber." The main reasons for his rejection of this mix were, firstly, that the water absorption was affected by changes in the time of vulcanisation and secondly, that the temperature of vulcanisation was lower than that commonly used in practice. He chose for test-purposes a 92.5 : 7.5 rubber-sulphur mix but his figures do not indicate that this mix has any particular advantage over the mercaptobenzothiazole mix when testing normal rubber. Using purified rubber in the rubber-sulphur mix there is less variation in water absorption for different times of cure than in the mercaptobenzothiazole mix but this is probably due to the comparative ineffectiveness of increased times of cure in a rubber devoid of natural or added accelerators of vulcanisation and it is known that "tight" curing causes a reduction in water absorption. Van Dalfsen's objection to curing at 127°C. (20 lb./sq. in. steam) is questionable, for much technical curing with mercaptobenzothiazole mixings is done at this temperature and in any case an equivalent state of cure would be attained by a reduction in time if a higher temperature were used. It could be objected more strongly that a rubber-sulphur mix is not representative of current commercial practice.

As a result of water-absorption tests upon a large number of rubber samples cured in the mercaptobenzothiazole mix it has been found that good agreement with conclusions drawn from tests upon the crude rubber can be obtained and the A.C.S. mercaptobenzothiazole mixing is considered to be suitable for comparative testing and routine evaluation.

THE TEST-PIECE

The moulds intended for crude rubber and described under "The preparation of test-pieces" were found to be quite suitable for vulcanised rubber. Sheets are vulcanised in these moulds and are cut into three strips of size $4 \times 1 \times 0.08$ inches. The thickness is 0.08 inch within limits which do not warrant correction (vulcanised rubber does not recover thickness on release of pressure as does un-vulcanised rubber).

CALCULATION OF WATER ABSORPTION

After immersion a vulcanised sample does not contract and the absorption is therefore calculated on the total surface area, which is equal to $(8+10t)$ sq. inches, where t is the gauge in inches. Then, if W is the weight of water absorbed in milligrams,

$$\begin{aligned}\text{Absorption by vulcanised rubber} &= \frac{W}{8+10t} \\ &= \frac{W}{8.8} \text{ mg./sq. in.}\end{aligned}$$

since t may be considered a constant gauge of 0.08 inch for vulcanised rubber when using the moulds described.

TIME OF VULCANISATION

Using the A.C.S. "Captax" formula the effect of increasing the time of vulcanisation is to cause a reduction in water absorption as indicated in Table IX.

TABLE IX

Effect of time of vulcanisation on water absorption

Sample No.	Mean absorption after immersion for 20 hours at 70°C. (mg./sq. in.)			Mean absorption after immersion for 14 days at 90°F. (mg./sq. in.)		
	81	82	5455	81	82	5455
Time of vulcanisation at 127°C.						
20 minutes	7.1	7.4	10.5	8.0	8.7	14.6
30 "	6.9	7.6	10.7	7.5	7.7	14.2
40 "	6.9	7.2	9.5	7.0	7.0	14.2
60 "	6.1	6.6	9.6	6.4	7.3	13.2
80 "	6.3	5.9	9.3	5.9	6.4	12.5
100 "	6.1	6.0	8.9	5.8	6.2	12.4

For routine testing a single curing time was required and 60 minutes at 127°C. was selected but a complete evaluation necessitates testing over a range of cures in conjunction with other tests on the vulcanisates.

SUMMARY OF THE METHOD OF EVALUATING THE WATER-ABSORPTION CAPACITY OF VULCANISED RUBBER

- (1) Compound the sample using the A.C.S. "Captax" mixing. Sheet to a thickness of approximately 0.1 inch and stand preferably for 24 hours.
- (2) Lay the sheet in a mould having a cavity depth of 0.08 inch.
- (3) Vulcanise at 127°C. for 60 minutes (or a range of curing times if required).
- (4) Remove the vulcanised sheet from the mould, cool, and stand for 24 hours.
- (5) Place on paper and cut three 4×1 inches test-pieces per sample (trimming board or die).
- (6) Attach each test-piece to a glass sinker and immerse in distilled water previously brought to the testing temperature.
- (7) Keep in a thermostatically-controlled atmosphere for 20 hours at 70°C. and/or for 14 days at 90°F.
- (8) Allow the tubes and contents to cool at atmospheric temperature for about half an hour, or cool in any convenient manner to avoid losses when weighing.
- (9) Remove each test-piece just prior to weighing; wipe dry with a lintless cloth and weigh within two minutes.
- (10) Place in an oven maintained at about 90°C. until dry and re-weigh.
- (11) Calculate the result from the formula:—

$$\text{Water absorption in mg./sq. in. of surface} = \frac{W}{8.8}$$

where W is the decrease of weight on drying, in milligrams.

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NOTE ON THE PRODUCT OF A REACTION BETWEEN AQUA REGIA AND LATEX

BY

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Summary

Details are given of a method by which latex may be caused to react with a mixture of nitric and hydrochloric acids to form a free-flowing powder. Some of the chemical and physical properties of the product are described.

Arising from experiments to repeat on fresh latex the halogenation experiments made by H. C. Baker (1938) on ammoniated latex, the sodium chlorate and hydrochloric acid reagents were replaced by *aqua regia*. After numerous unsuccessful trials with different stabilisers and combinations of mixed acids a method was evolved which produces a product in the form of a fine free-flowing powder. R. L. Sibley (1941) stated in a recent lecture that a wide variety of products could be obtained from rubber by reaction with increasing proportions of *aqua regia* and this note gives the details of a method of producing an interesting product by the action of *aqua regia* upon rubber in the form of fresh latex.

Method

In a water bath arranged to admit a flow of cold water, set up a six-litre bolt-head flask fitted with a mechanical stirrer and a dropping funnel. Place 100 ml. of fresh latex (35-40 per cent dry-rubber-content) in the flask and stir in 24 grams of "Lissapol A" paste mixed with 200 ml. of water, followed by 600 ml. of concentrated hydrochloric acid. The temperature of the water surrounding the flask should be about 50°C. initially and when the contents reach this temperature 150 ml. of concentrated nitric acid are run rapidly from the dropping funnel into the latex mixture with constant stirring. The reaction gradually gathers momentum and the water in the bath heats up rapidly if not changed, but by admitting a steady stream of cold water to the bath the reaction can be controlled and the temperature of the reactants kept down to about 80°C. Copious fumes of nitrogen peroxide are at first evolved but when these have subsided the water is run out of the bath and the reaction mixture allowed to stand overnight.

The product is a fine yellowish-brown powder which settles readily and is easily washed by decantation, finally filtered on a Buchner funnel and dried in a vacuum desiccator.

OBSERVATIONS MADE DURING THE DEVELOPMENT OF THE METHOD

If the above procedure is used with the exception that the temperature of the reacting mixture is kept below 10°C. by the use of ice, the product is not homogeneous—part is rubbery and the remainder has the texture of brown factice. If the initial temperature is not more than 25°C., the reaction temperature does not rise above 30°C. and a brown coagulum forms. The addition of the nitric acid before the hydrochloric acid is not as effective as the order recommended.

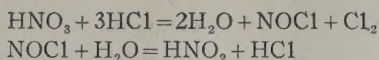
It was thought that the reaction might be more readily controlled if the latex was at a sufficiently high temperature to cause instantaneous reaction, and experiments were made accordingly.

Latex in the presence of "Lissapol A" and hydrochloric acid coagulated when the temperature approached 100°C.; when the acid was omitted a thick paste formed at that temperature. Latex and stabiliser without acid remained liquid at 80°C. but hard lumps were formed when the previously mixed hydrochloric and nitric acids were added. At 70°C. in the presence of hydrochloric acid and stabiliser the latex remained fluid but on addition of nitric acid coagulation occurred. Commencing with the latex and acid mixture at 60°C. all the nitric acid was added before flocculation occurred but lumps were formed when the vigorous reaction set in. However, it was found that these lumps readily broke down to a fine powder on a Buchner funnel. An initial temperature of 50°C. was found to be best. Doubling the amount of stabiliser did not appreciably increase the stability of the mixture.

Other variations included running the cold stabilised latex and hydrochloric acid mixture into the nitric acid at 80°C. This was fairly successful; the product looked more granular but was easily pressed to a fine powder. Inter-changing the acids and running a latex-nitric acid mixture into hot hydrochloric acid was unsuccessful, a mixture of brown and yellow granules being produced. The stabiliser sold as "Vulcastab" was found to be suitable but "Vultamol," casein and saponine were not.

The Reaction

Goldschmidt's equations for the reaction between nitric and hydrochloric acids in the presence of water are given below but these do not fully represent the more complex reactions which occur (Mellor 1922).



The reagents present provide possibilities for numerous reactions with rubber; Baker (1938) has produced products with nascent chlorine under similar conditions; nitrosyl chloride will also attack the double bonds of the rubber molecule and the acids are possible additive groups. In addition, oxides of nitrogen and products of side reactions not represented by the above general equations are likely still further to complicate the reaction.

Properties of the Product

The product is a yellowish-brown free-flowing powder having more than double the weight of the original rubber in the latex. Ultimate analyses have not been made but chlorine was estimated in the Parr Bomb and nitrogen by Kjeldahl; typical results are N=5.3 per cent, Cl=26.1 per cent. It has not been ascertained whether the stabiliser contributes to the yield but if it does not the oxygen content of the product should be of the order of 20 per cent.

The powder is insoluble in water and sodium carbonate solution but soluble in caustic soda solution, changing to a dark brown on contact with the alkali. It is insoluble in dilute sulphuric acid but dissolves in the cold concentrated acid without decomposition. In aqueous ammonia it is only partially soluble and when filtered the residue on the filter paper dissolves in acetone but gives a much darker solution than the original powder. It does not decolorise bromine in carbon tetrachloride solution.

On warming to 80°C. the product softens and can be pulled out into brittle threads, but at 130°C. thermal decomposition sets in with rapid generation of heat and carbonisation of the mass.

The following is a table of solubility in organic solvents:—

Solvent	Solubility
1. Acetone	Soluble
2. Ethyl Acetate	Soluble
3. Ethyl lactate	Soluble
4. Butyl phthalate	Soluble
5. Ethylene glycol mono- ethylether	Soluble
6. Triacetin	Soluble
7. Cyclohexanone	Soluble
8. Amyl Acetate	Small insoluble portion

Solvent	Solubility
9. Butyl Acetate (iso)	Small insoluble portion
10. Butyl Acetate (normal)	Small insoluble portion
11. Tri cresyl phosphate	Small insoluble portion
12. Ethyl alcohol	Partially or slightly soluble
13. Cyclohexanol	Partially or slightly soluble
14. Amyl acetate	Partially or slightly soluble
15. Chloroform	Partially or slightly soluble
16. Ether	Insoluble
17. Petroleum ether	Insoluble
18. Benzene	Insoluble
19. Toluene	Insoluble
20. Xylene	Insoluble
21. Cyclohexane	Insoluble
22. Dekalin	Insoluble
23. Tetralin	Insoluble
24. Carbon tetrachloride	Insoluble
25. Trichlorethylene	Insoluble
26. Tetrachlorethane	Insoluble
27. Monochlorbenzene	Insoluble
28. Carbon di-sulphide	Insoluble

After storage for two years a slight acrid odour and a darkening in colour is noticeable but the general properties of the powder appear to be unchanged. Numerous possible technical applications appear to be worthy of investigation.

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